



Leaching of waste battery paste components. Part 1: Lead citrate synthesis from PbO and PbO₂

M.S. Sonmez^{a,*}, R.V. Kumar^b

^a Department of Materials & Metallurgical Engineering, Faculty of Chemistry & Metallurgy, Istanbul Technical University, 34469, Maslak, Istanbul, Turkey

^b Department of Materials Science and Metallurgy, University of Cambridge, United Kingdom

ARTICLE INFO

Article history:

Received 30 October 2007

Received in revised form 24 April 2008

Accepted 26 April 2008

Available online 3 May 2008

Keywords:

Spent battery pastes

Leaching/crystallisation

Lead citrate

Characterisation

Recycling

ABSTRACT

In this study, as part of developing a new process which can avoid smelting and electro-winning, citric acid based reagents in aqueous media were reacted with PbO and PbO₂. These two oxides are important components in the spent lead-acid battery paste and together account for up to 50% of the paste by weight. PbSO₄, the main component in a spent battery paste accounting for the remaining 50%, is dealt with in Part 2 in a separate paper. Reaction between PbO and C₆H₈O₇·H₂O or PbO₂ with a mixture of C₆H₈O₇·H₂O and H₂O₂ yielded lead citrate, Pb(C₆H₆O₇)·H₂O, which was characterised by XRD, SEM and FT-IR analysis. Optimal synthesis conditions were determined by investigating the effect of time, temperature, concentration, and the starting Pb oxide/water ratio. The optimal condition for leaching a mol of PbO at room temperature (20 °C) was found to be: 1 mol of (C₆H₈O₇)·H₂O solution; 1/3 as the starting PbO/water ratio and 15 min of reaction time. Pure citrate product, Pb(C₆H₆O₇)·H₂O was rapidly crystallized from the solution, in the leaching process. Leaching of PbO₂ required the use of a mild reducing agent. For each mole of PbO₂, the optimum condition at 20 °C was found to be: a solution containing 4 mol of C₆H₈O₇·H₂O and 2 mol of H₂O₂; 1/5 as the starting solid PbO₂/water ratio; and 60 min of reaction time. The product, as with PbO, was pure Pb(C₆H₆O₇)·H₂O compound. The remaining lead content of the filtrate solution was 0.017% and 1% corresponding to recoveries of 99.98% and 99% of lead as citrate, after the leaching/crystallization/filtration process with PbO and PbO₂, respectively. Asymmetric stretching vibrations between 1599 and 1662 cm⁻¹, whereas symmetric vibrations between 1520 and 1327 cm⁻¹ for lead citrate synthesised from PbO and asymmetric stretching vibrations between 1600 and 1642 cm⁻¹ as well as symmetric vibrations between 1517 and 1326 cm⁻¹ for the product obtained from PbO₂ revealed the strong IR adsorptions associated with a carboxylate structure. XRD data was identical to the well documented crystalline Pb(C₆H₆O₇)·H₂O compound from both the oxides. SEM revealed the formation of plate/sheet like morphologies. The difference in the column size of the Pb(C₆H₆O₇)·H₂O formed from the two lead oxides can be related to difference in the rate of the respective reactions.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Lead compounds have attracted scientific interest not only for their coordination properties and stereochemistry, but also for their toxicity effect on human beings (Harrison and Steel, 1982; Kourgiantakis et al., 2000; Burford et al., 2004). Separately, lead-acid batteries constitute the single most consumption of lead at over 70% of all the lead produced (Prengaman, 2000). Considering the much publicized toxic properties of lead, efficient recycling or recovery from waste materials, is a critical necessity for ecological reasons.

Either pyrometallurgical or hydro-electrometallurgical methods have been used for the treatment of scrap battery pastes (Habashi, 1997; Prengaman et al., 2001). While pyrometallurgical methods still comprise over 90% of the recovery technology, they are under severe

criticism, especially due to SO₂ emission from the need to decompose PbSO₄ at elevated temperatures of >1000 °C, and lead emissions from fuming at these high temperatures. Given the environmental concerns in recent years, hydro-electrometallurgical processes have been developed recently. One of the basic problems during hydro-electrometallurgical treatment methods is the low solubility of lead compounds in solvents as well as inefficient desulphurisation in the aqueous solution.

In the most common approach, the battery paste is charged into smelting furnaces (Prengaman, 1980; Forrest and Wilson, 1990). New developments in smelting technology have led to recycling in processes such as Isasmelt (Ramus and Hawkins, 1993; Ahmed, 1996) or short rotary furnaces (Forrest and Wilson, 1990). The paste material contains a large proportion of sulphur in the form of sulphate which results in the well documented SO₂ problems and all that this entails (Harrison, 2000). Decomposition of PbSO₄ requires the use of relatively high temperatures (Habashi, 1997). High temperature

* Corresponding author. Tel.: +90 285 33 99; fax: +90 212 285 34 27.

E-mail address: ssonmez@itu.edu.tr (M.S. Sonmez).

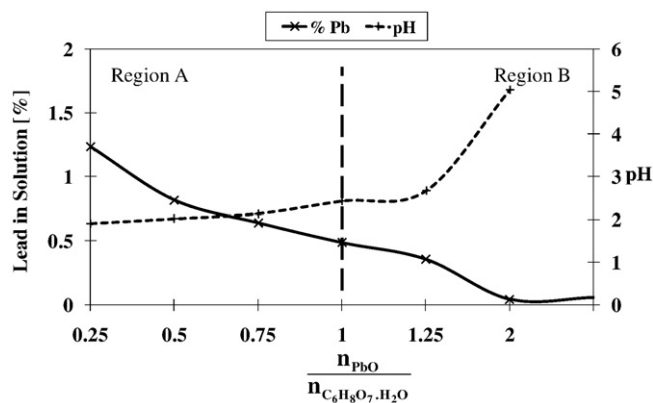


Fig. 1. Lead content and pH change of the solution after filtering for different initial α ratio (constant leaching conditions: 60 min, 250 rpm, 20 °C). (Region A: pure $\text{Pb}(\text{C}_6\text{H}_8\text{O}_7) \cdot \text{H}_2\text{O}$, Region B: contaminated $\text{Pb}(\text{C}_6\text{H}_8\text{O}_7) \cdot \text{H}_2\text{O}$).

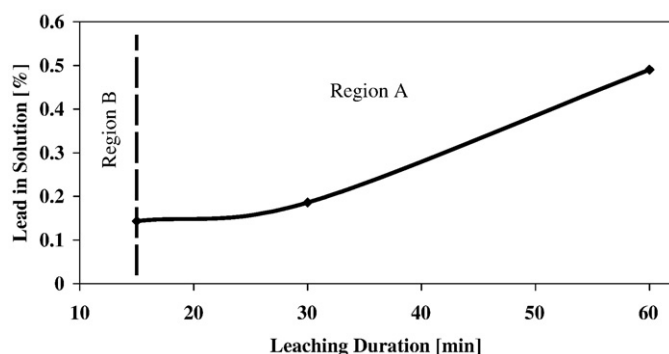


Fig. 2. Lead content of the solution after filtering as a function of leaching duration (leaching conditions: α : 1, starting PbO /water ratio: 1/5, 250 rpm, 20 °C).

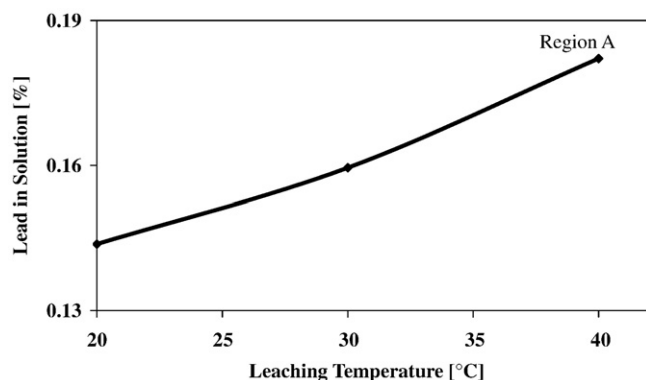


Fig. 3. Lead content of the solution after filtering for different leaching temperatures (constant leaching conditions: 15 min, α : 1, starting PbO /water ratio: 1/5, 250 rpm).

process also generates significant amounts of hazardous lead bearing fumes, dust and slag. When Fe is used to fix S in the paste, hazardous FeS-PbS matte is also produced. Disposal of lead bearing waste products is not only expensive but also harmful to the environment. Smelting processes are energy intensive, generate NO_x and have high operating costs. Utilization of Na_2CO_3 as a high temperature sulphur fluxing agent produces either Na_2SO_4 (in the slag) or $\text{FeS-Na}_2\text{S}$ soda matte. While SO_2 gaseous emission problem is abated, water leachable hazardous waste products are produced. It must be noted that for a number of environmental and cost factors, the smelting capacity in many industrial countries are being relocated to newly industrial countries.

Given the serious problems encountered in the smelting route for recycling lead battery paste, several research, pilot scale and commercial methods using hydrometallurgical approach have been developed. Hydrometallurgical methods have been used to remove S in the paste as soluble Na_2SO_4 (aq) or $(\text{NH}_4)_2\text{SO}_4$ (aq) using Na_2CO_3 (aq), NaOH (aq) or $(\text{NH}_4)_2\text{CO}_3$ (aq) solutions (Prengaman and Raymond, 1980; Reynolds et al., 1990; Gong et al., 1992; Prengaman et al., 2001). Na_2SO_4 is then crystallized from the remaining solution and can be sold off as a by-product. The insoluble product PbCO_3 or $\text{Pb}(\text{OH})_2$ collected in the form of sludge or filter cake is then routed to the smelter. A number of new plans are under development for future application. Despite extensive effort, it has not yet been possible to avoid the retention of a substantial amount of sulphur in the lead-bearing product and thus the smelter SO_2 problem is not fully abated.

In order to evade the use of smelting altogether, the insoluble sludge or filter cake from the above hydrometallurgical desulphurisation process may be dissolved in fluoroboric acid (HBF_4) (Olper, 1993). While PbCO_3 or $\text{Pb}(\text{OH})_2$ are soluble in HBF_4 , the other important constituent of the paste PbO_2 is not and has to be reduced in the solution to $\text{Pb}(\text{II})$ by using H_2O_2 (aq). Both PbO and Pb are soluble however. The solution is then purified by cementation followed by electro-winning. In this variation a large number of steps are required making the process expensive. Electro-winning process is capital intensive and is often only suitable for large scale operations which in turn entail large scale movement of battery waste materials.

In another variation of the hydrometallurgical/electro-winning method, both PbCO_3 and PbO_2 are converted to PbO by a calcination/reduction step. PbO is then solubilised in H_2SiF_6 (aq) from which Pb is electro-won (Prengaman, 1995). More expensive and even more complex process involve the use of leaching in stages with HCl , NaCl and $\text{Ca}(\text{OH})_2$ solutions so that S is removed as gypsum, while Pb is transferred as PbCl_2 from which Pb is electro-won using an energy

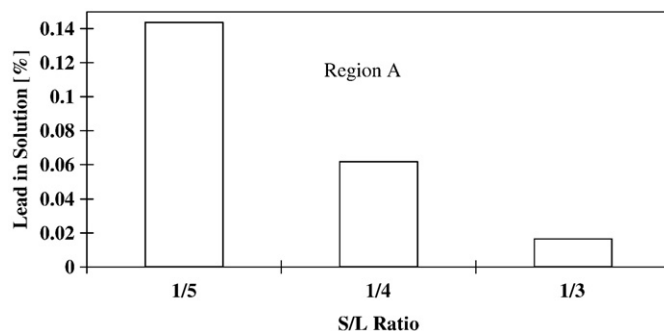


Fig. 4. Lead content of the solution after filtering for different starting PbO /water ratios (constant leaching conditions: 15 min, α : 1, 250 rpm, 20 °C).

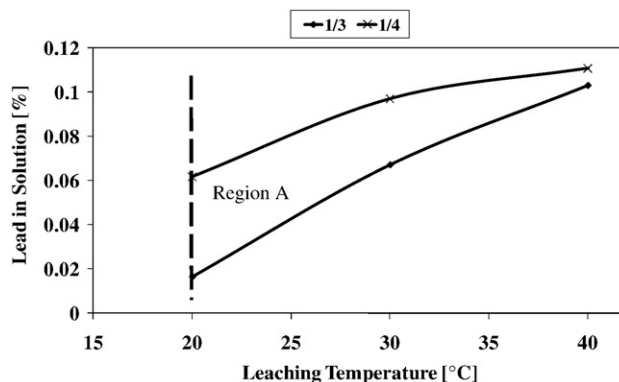


Fig. 5. Lead content of the solution after filtering for different temperatures and starting PbO /water ratios (constant leaching conditions: 15 min, α : 1, 250 rpm).

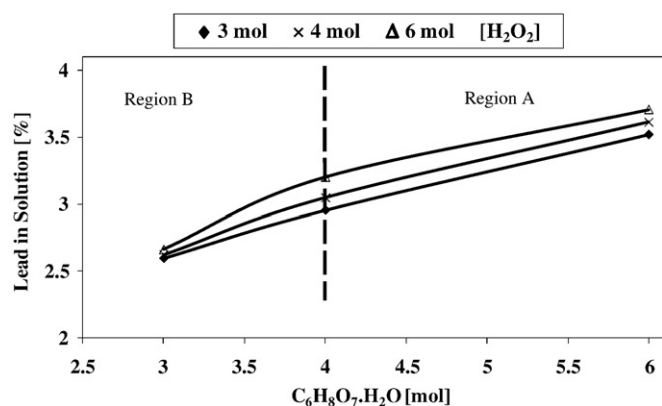


Fig. 6. Lead content of the solution after filtering for different initial $C_6H_8O_7 \cdot H_2O$ and H_2O_2 amounts per mol of PbO_2 (leaching condition: 60 min, 250 rpm, starting PbO_2 /water ratio: 1/50, 20 °C). (Region A: pure $Pb(C_6H_6O_7) \cdot H_2O$, Region B: contaminated $Pb(C_6H_6O_7) \cdot H_2O$).

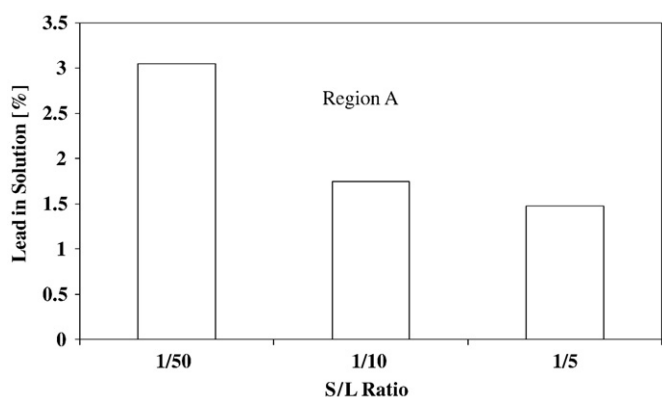


Fig. 7. Lead content of the solution after filtering for different starting PbO_2 /water ratio ratios (constant leaching conditions: 60 min, 250 rpm, 4 mol of $C_6H_8O_7 \cdot H_2O$ and 4 mol of H_2O_2 for 1 mol of PbO_2 , 20 °C).

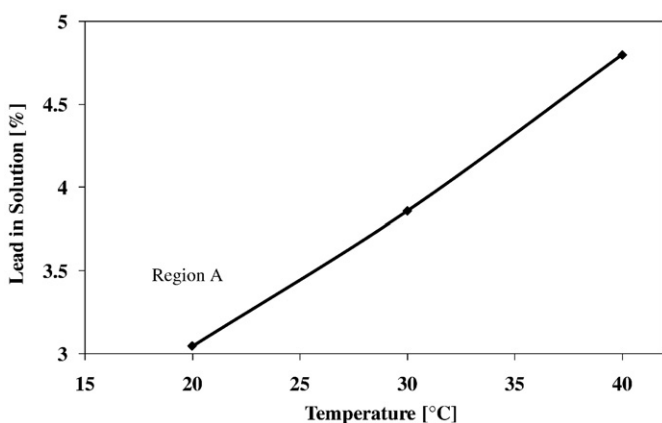


Fig. 8. Lead content of the solution after filtering for different temperatures — all data correspond to Region A (constant leaching conditions: 60 min, 250 rpm, starting PbO_2 /water ratio=1/50, 4 mol of $C_6H_8O_7 \cdot H_2O$ and 4 mol of H_2O_2 for per mole of PbO_2).

intensive diaphragm electrochemical cell (Diaz and Andrews, 1996; Andrews et al., 2000).

It is quite clear that despite the availability of excellent recycling infrastructure for the lead battery, there is a need for a simpler and a more benign route in the face of tougher legislations and cost competitiveness. It is attractive to invent a cost effective process that does not involve smelting or electro-winning. Most importantly, despite stringent legislations, the successful record for lead recycling

must be maintained. There has been a recent tendency to ship a significant proportion of lead wastes across continents to sustain recycling in order to minimise any local environmental costs. This practice may not be sustainable in the long run. An environmentally sound process that can be operated on a small scale as well as in large plants will be in demand.

In this paper we are reporting that the lead can be converted to a crystalline salt, $Pb(C_6H_6O_7) \cdot H_2O$ (lead citrate), which in turn can form the precursor for extracting lead from lead-waste materials. In this paper, lead oxides PbO (lead monoxide) and PbO_2 (lead dioxide), present as important components in spent lead acid battery pastes, are considered. The principle is also relevant for treating lead oxides in paints, monitors and solders. Leaching/crystallization behaviour of $PbSO_4$ — the major component in the lead-battery waste — is reported in Part II (Sonmez and Kumar, 2009).

2. Materials and methods

Analytically pure and commercially available chemicals were used to model the components in a spent battery paste. Leaching experiments were carried out by using lead oxide (PbO , Acros Organics), lead dioxide (PbO_2 , Fisher Scientific) and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, Acros Organics) as starting materials. During the leaching/crystallization experiments with PbO_2 , hydrogen peroxide (H_2O_2 , Aldrich) 27.5% solution in water was used for reducing the dioxide.

Leaching procedure was carried out by stirring the mixture with a magnetic stirrer at a constant stirring rate of 250 rpm in a glass beaker.

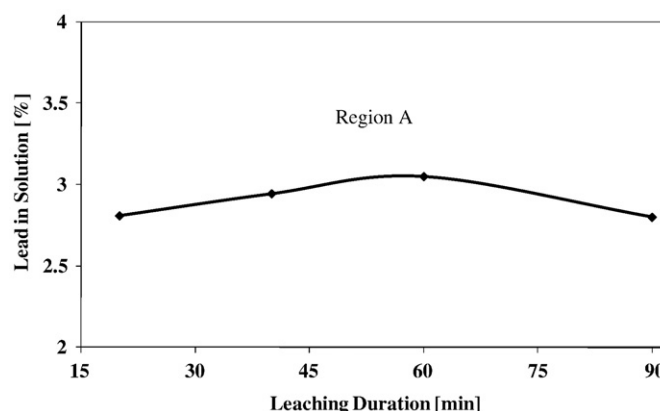


Fig. 9. Lead content of the solution after filtering for different leaching durations — all data correspond to Region A (constant leaching conditions: 250 rpm, starting PbO_2 /water ratio: 1/50, 4 mol of $C_6H_8O_7 \cdot H_2O$ and 4 mol of H_2O_2 per mol of PbO_2 , 20 °C).

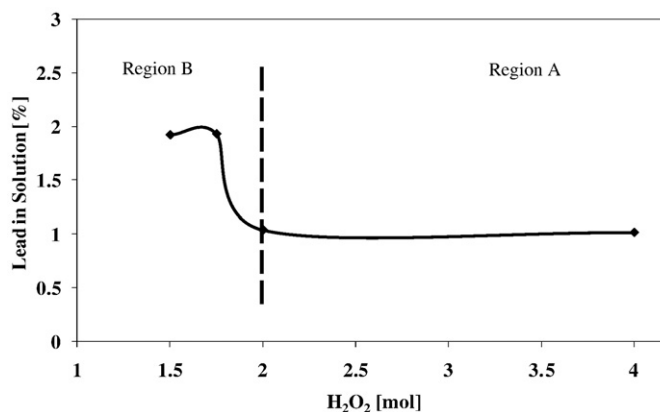


Fig. 10. Lead content of the solution after filtering for different initial H_2O_2 amounts (constant leaching conditions: 60 min, 250 rpm, starting PbO_2 /water ratio: 1/50, 4 mol of $C_6H_8O_7 \cdot H_2O$ for 1 mol of PbO_2 , 20 °C).

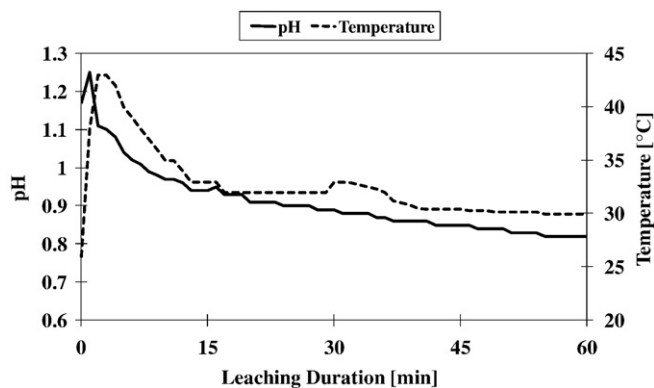


Fig. 11. pH and temperature change during the leaching of PbO_2 (4 mol of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and 2 mol of H_2O_2 for 1 mol of PbO_2).

Synthesis conditions were determined by experimenting different mol ratios of the lead compounds and the reactants. Reaction temperature of the mixture was monitored by a contact thermometer.

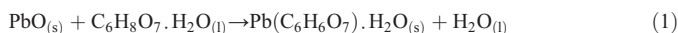
The analysis of the filtrate solution for lead was performed by ICP-AES (Varian Liberty AX Sequential ICP-AES). The X-ray diffraction (XRD) spectra were obtained using Philips X-ray diffractometer ($\text{Cu K}\alpha$, 40 kV, 25 mA, calibrated with Si-standard). The raw materials and the end products were characterised by FT-IR (Tensor 27, Bruker Optics). The morphology of the material was examined by field emission scanning electron microscopy (FESEM-JEOL 6340F).

Leaching/crystallization experiments were carried out in order to optimize the mol ratio of the reactants, the temperature and the duration of the process. Leaching/crystallization efficiencies of PbO with $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and PbO_2 with the mixture of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ plus H_2O_2 were calculated from the lead content of the filtrate solution. Recovery of lead as uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ was calculated from the experimental data.

3. Results and discussion

3.1. Lead citrate synthesis from PbO

One of the three main components of the scrap battery paste, PbO , (others being PbO_2 and PbSO_4) was leached with an aqueous solution of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$. Lead citrate was rapidly crystallized in the solution. The reaction can be represented by the following Eq. (1).



Leaching and crystallization behaviour of PbO in $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ solution was optimized by considering initial $\frac{n_{\text{PbO}}}{n_{\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}}} (\alpha)$ ratio; leaching duration; leaching temperature; S/L ratio, defined as initial wt of PbO /initial wt of water; and the pH of the solution. At $\alpha=1$, and a PbO /water ratio of 1/3, the concentration of citric acid is 1.5 M. As the ratio of PbO /water is decreased from 1/3 to say 1/5, the starting concentration of citric acid is correspondingly decreased to 0.9 M. The precipitation of pure lead compound was the main objective of the experiments. Any contamination of the

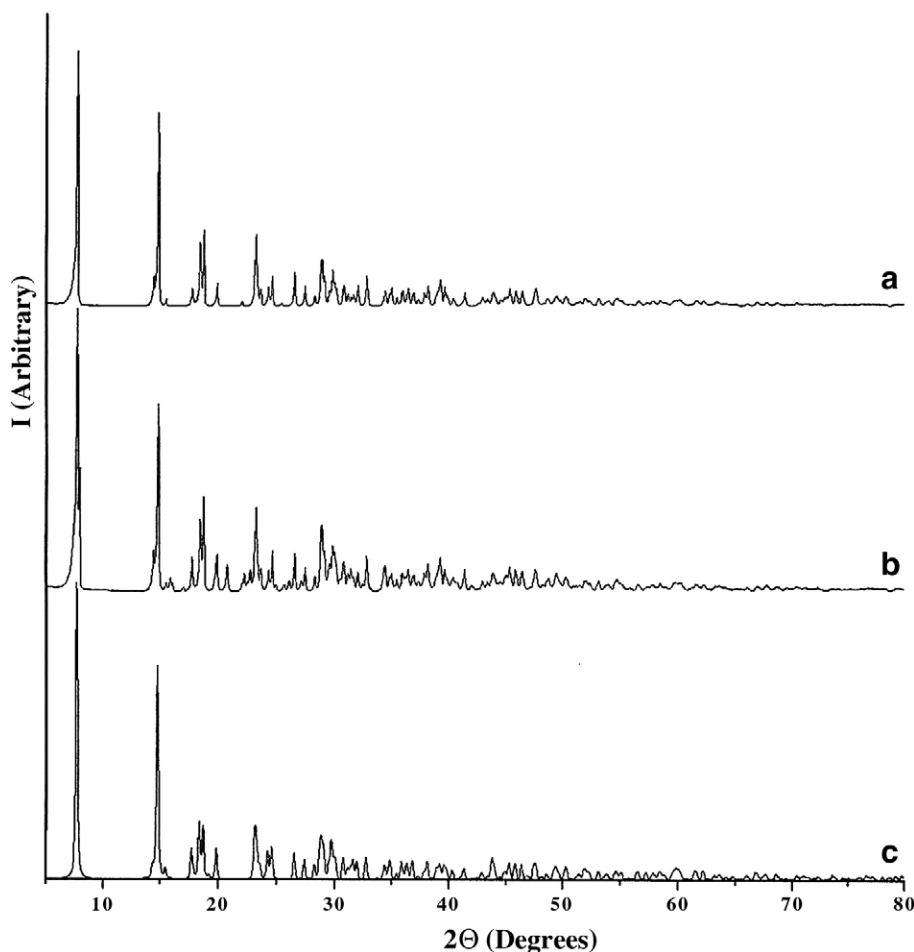


Fig. 12. Comparison of X-ray diffraction analysis of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ a) created from Kourgiantakis et al. (2000), b) produced from PbO -leaching conditions: α : 1, starting PbO /water ratio: 1/3, 250 rpm, 20 °C, 15 min, and c) produced from PbO_2 -leaching conditions: solution containing 4 mol of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and 2 mol H_2O_2 , starting PbO_2 /water ratio: 1/5, 250 rpm, 20 °C, 60 min, data in b and c, correspond to materials in region A.

citrate product is not desirable, especially as this represents incomplete reaction of the lead oxides. It must be noted that the regions of pure $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7)\cdot\text{H}_2\text{O}$ precipitate and regions of contaminated $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7)\cdot\text{H}_2\text{O}$, as deduced from XRD, are clearly separated and marked in the relevant figures as Region A and Region B, respectively. The XRD results will hereafter be discussed in the text.

As α ratio is increased together with an increase in PbO/water ratio (from 1/20 to 1/2), lead content of the solution is found to decrease due to

insufficient $\text{C}_6\text{H}_5\text{O}_7\cdot\text{H}_2\text{O}$ during the leaching process (Fig. 1, Region B). Although lead content of the solution was decreased when α ratio was increased, at α ratio greater than 1, non-reacted PbO remained in the precipitate even after 60 min. Furthermore increasing the initial PbO content with respect to the initial $\text{C}_6\text{H}_5\text{O}_7\cdot\text{H}_2\text{O}$ amount resulted in higher pH values of filtrate solution due to consumption of the acid. It should be noted that for maximising recovery of lead in the form of citrate it is important to minimise the lead content in the solution and simultaneously

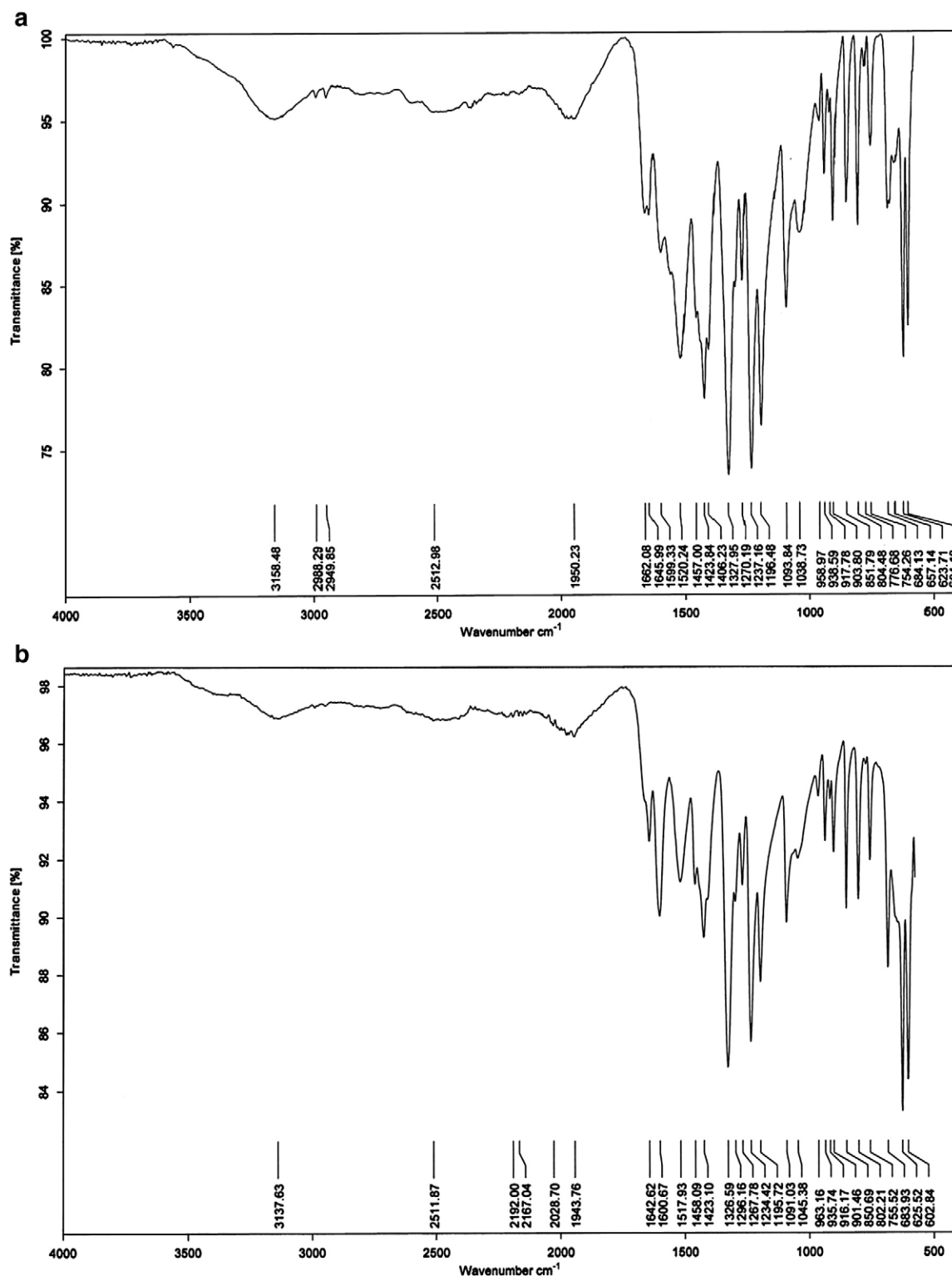


Fig. 13. FT-IR spectra of $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7)\cdot\text{H}_2\text{O}$ produced from both a. PbO and b. PbO_2 .

maximise the formation of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ product. As long as the filtrate consists of only $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ (with negligible retained/unreacted PbO), lower lead content in the filtrate solution will correspond to a higher recovery. It is also easier for recycling and or even disposing (but not recommended) the spent liquor containing lower levels of lead. Pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ precipitation could be achieved up to the bordered line as shown in Fig. 1 (Region A). It can be seen from Fig. 1, that the optimal condition for the leaching is realized for $\alpha=1$ corresponding to a minimum lead content in the filtrate solution.

Complete precipitation conversion was not achieved and unreacted PbO particles remained in the precipitate up to 15 min of leaching as indicated by Region B in Fig. 2. The amount of lead in the filtration solution was 0.14 wt wt.% after 15 min. The product can re-dissolve as shown by the higher lead content in the solution for longer leaching durations (0.5% for 60 min) due to the dissolution of recently formed $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ particles (Fig. 2, Region A). In order to maximise recovery of lead from the solution, it is important to optimise the duration of leaching and crystallization. Thus it can be noted that excessive leaching duration is counter-productive for recovery of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$. By decreasing the duration, the recovery was further enhanced from 99.5 to 99.85%.

There was no significant effect of leaching temperature on both the precipitation and lead content of the filtration solution as shown in Fig. 3 for the leaching time of 15 min. Lead content of the solution increased up to 0.18% at 40 °C reflecting the very small increase in dissolution with temperature. The product was pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ under all the conditions in this experiment (XRD data for pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ from PbO are shown in Fig. 12b and discussed in Section 3.3).

Lowest lead content of the solution (0.017%) after filtration was achieved by leaching with a starting PbO /water ratio of 1/3 (Fig. 4), together with maximum recovery of 99.98% as pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ product. Uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ was formed for the range of S/L ratios shown. Addition of too much water can decrease the reactivity by diluting the citric acid, while too little water can be detrimental for providing the leaching media.

Marginally increasing dissolution behaviour was also observed for different starting PbO /water ratios similar to Fig. 3 when the leaching temperature was increased up to 40 °C as shown in Fig. 5. Thus a lower temperature (room temperature) and a S/L ratio of 1/3 is preferred for optimal leaching and crystallization leading to a maximal recovery of uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ product.

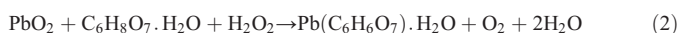
3.2. Lead citrate synthesis from PbO_2

PbO_2 is relatively a difficult compound to dissolve in aqueous media. It was found necessary to reduce this with a reducing agent such as H_2O_2 . PbO_2 was leached by $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and H_2O_2 , to precipitate lead citrate, $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$. The parameters, relative amounts of H_2O_2 , tempera-

ture, duration, relative concentrations of the reagents and pH were investigated to optimise the leaching process.

PbO_2 could not be effectively leached and precipitated with citric acid by itself. Although the lead content of the solution was increased up to 3.5% after filtering but the filtrate mainly contained PbO_2 with a very small amount of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$. When only H_2O_2 solution was used for reacting with pure PbO_2 , filtrate remained as unreacted PbO_2 after filtering with a small amount of (0.005% of Pb) in the solution at both 20 °C and 40 °C even after 60 min. Results reported by Ferracin et al. (2002), on the reaction between PbO_2 and citric acid showed that very long leaching duration was needed for achieving any significant solubility.

H_2O_2 was effective as a reducing agent and assisted leaching with $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ resulting in precipitation of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$. The suggested reaction is as follows:



It was found that combined with the assistance of H_2O_2 , a minimum concentration of 4 mol of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ per mol of PbO_2 was required to fully leach PbO_2 and precipitate uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ product (Fig. 6). (XRD data of pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ formed from PbO_2 are shown in Fig. 12c and further discussed in Section 3.3). For the best condition in Fig. 6, the calculated lead recovery as uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ is about 97.2%. Initially a large amount of water was used relatively to the reagent ($S/L=1/50$), thus the reagents were dilute. Subsequently, the relative amount of water was decreased and S/L ratio of 1/5 was found to produce better recovery for uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$. A relatively high $\text{H}_2\text{O}_2/\text{PbO}_2$ molar ratio (>2) was also required to produce uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ precipitate.

Uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ was obtained after all the experiments in Fig. 7. When the starting PbO_2 /water ratio was increased to 1/5 for a more concentrated solution, lead content of the solution was decreased to 1.5% indicating improved lead recovery at 98.5%. With increasing starting temperature the lead content of the solution increased to 4.8% for the experiment at 40 °C (Fig. 8), with a lower recovery of 95.2%. This may be related to an enhanced solubility at elevated leaching temperatures. In order to achieve uncontaminated $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$, under the following leaching condition: a temperature of 20 °C; stirring rate of 250 rpm; starting PbO_2 /water ratio of 1/50; 4 mol of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and 4 mol of H_2O_2 per mol of PbO_2 , as specified in Fig. 9, the minimum reaction time was found to be approximately 60 min. The region A corresponding to time >60 min is required for forming pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ from the leaching solution, while region B at <60 min is the contaminated region. Recovery is slightly increased with increasing time as can be calculated from the lead in solution data shown in Fig. 9. Fig. 10 showed that when the initial H_2O_2 amount was increased, lead content of the solution was decreased accompanied by an efficient

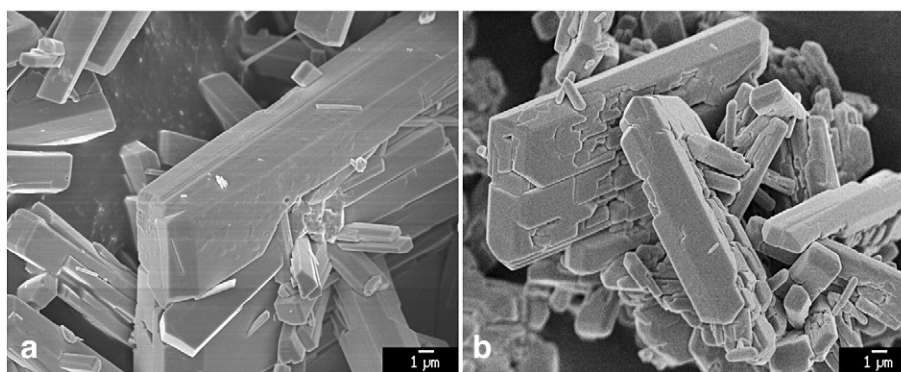


Fig. 14. SEM images of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7) \cdot \text{H}_2\text{O}$ produced from both a. PbO ($\times 4000$) leaching conditions: — α : 1, starting PbO /water ratio: 1/3, 250 rpm, 20 °C, 15 min and b. PbO_2 ($\times 4300$) leaching conditions: solution containing 4 mol of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ and 2 mol H_2O_2 , starting PbO_2 /water ratio: 1/5, 250 rpm, 20 °C, 60 min.

precipitation of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$. Although complete consumption of H_2O_2 is expected from stoichiometry for 1 mol of H_2O_2 per mol of PbO_2 the $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ product was not pure as revealed by X-ray diffraction analysis. Pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ without any contamination was obtained only at a minimum of 2 mol of H_2O_2 was reacted with 4 mol of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ for each mol of PbO_2 (Region A). The corresponding recovery is calculated as 99%.

Both $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and H_2O_2 had an effect of dissolving lead into the solution effectively followed by rapid precipitation of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$. Thus the combination of reagents is required to assist simultaneous reduction and leaching. Pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ was obtained after the filtration when only with the use of excess of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ (4 mol) and H_2O_2 during leaching (Region A in Figs. 6–10). Lead content of the solution increased to more than 3.5% when a very large excess for example 6 mol of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and 6 mol of H_2O_2 were used during leaching (Fig. 6). While the exact optimum values have not been ascertained, it is clear from Fig. 6 that 4 mol of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and 2–4 mol of H_2O_2 at S/L ratio of 1/5 can lead to pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ product for leaching at room temperature in >60 min with a negligible amount of lead remaining in solution after filtering the precipitate.

Although 1 mol of each starting reactants for the conversion of PbO_2 seem to be sufficient according to the Eq. (2), excess $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and H_2O_2 are required for the complete and efficient leaching and precipitation. The reason for this excess citric acid and H_2O_2 usage required is perhaps related to the temperature increase of the leaching solution at the beginning of the reaction. As shown in Fig. 11, exothermic reaction taking place in the initial stages of leaching results in a temperature increase of more than 40 °C within the first 3 min. This increase was followed by a gradual decrease with time. Oxygen evolution was observed which can be ascribed to the reducing effect of H_2O_2 . pH of the leaching media also increased rapidly in the first few minutes followed by a gradual decrease following similar trend as shown by the temperature changes. pH of the leaching media was still very acidic at 0.8 after 60 min, due to excess $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}/\text{H}_2\text{O}_2$ ratio.

The reaction sequence can be considered as reduction of PbO_2 by H_2O_2 followed by leaching of PbO . Reduction can be considered as the slower and the rate determining reaction, given the increased time required for PbO_2 in contact with PbO . H_2O_2 in contact with PbO_2 is a mild reducing agent and may necessitate the use of excess H_2O_2 to sustain the reduction. This is a matter of ongoing investigation. Thus when in-situ PbO is formed it must come in contact with $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ for leaching to proceed. It is not fully clear what role the increase in temperature has on leaching and crystallization reactions, but the need for excess citric acid requirement also is being further explored. Furthermore a side reaction between $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and H_2O_2 that can result in the formation of peroxy-acid which is a strong oxidizing agent can hinder the reduction reactions and may also lead to excess consumption of the reagents. The evidence for such a side reaction is being investigated but has been reported in the literature (Bettle et al., 1982).

3.3. Characterisation of lead citrate

X-ray diffraction data of the powders produced from the leaching of PbO and PbO_2 are shown in Fig. 12b and c, respectively. The existing X-ray diffraction analysis programs such as; Philips Highscore, Highscore Plus (X'Pert Plus Program for Crystallography and Rietveld Analysis, Philips Analytical B. V.) and PCPDFWIN (JCPDS-ICDD) did not contain any matching data. CIF (Crystallographic Information File) data of the study reported by Kourgiantakis et al. (2000) is available from Cambridge Crystallographic Data Centre by Crystal Web and X-ray diffraction pattern as shown in Fig. 12a.

Results as shown in Fig. 12, provide the confirmation that the synthesised powder from leaching of PbO by $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and PbO_2 by $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and H_2O_2 is $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$. FT-IR analyses have also revealed the strong adsorptions of carboxylate structure. Asymmetric stretching vibrations between 1599 and 1662 cm^{-1} , whereas sym-

metric vibrations between 1520 and 1327 cm^{-1} for the precipitate synthesised from PbO (Fig. 13a) and asymmetric stretching vibrations between 1600 and 1642 cm^{-1} as well as symmetric vibrations between 1517 and 1326 cm^{-1} for the product obtained from PbO_2 (Fig. 13b) belong to COO^- group. These results are compatible with carboxylate structures (Bellamy, 1980; Lin-Vien et al., 1991; Kourgiantakis et al., 2000).

Small variation in morphology of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ was revealed by SEM analysis between the two different starting materials, PbO (Fig. 14a) and PbO_2 (Fig. 14b). $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ synthesised from both PbO and PbO_2 had similar shape except for the size of columns averaging at 70 and 40 μm respectively. The difference between the sizes of the particles can be related to kinetic behaviour of the reactions. It is suggested that the bigger size of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ synthesised from PbO was produced in only 15 min duration probably controlled by diffusion, on the other hand with a longer period up to 60 min chemically controlled reaction promoted the leaching – precipitation of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ from PbO_2 . Much of the time may be associated with the slower reduction and leaching reaction rather than the precipitation of the citrate itself.

4. Conclusion

Leaching of pure PbO with 1 mol of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ solution per mol PbO for 15 min at 20 °C, with 1/3 as the ratio of starting PbO /water resulted in the crystallization of pure $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ crystals. The amount of lead remaining in the solution was 0.017% after crystallization, corresponding to an excellent recovery of 99.8%.

The leaching of pure PbO_2 with 4 mol of $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ and 2 mol H_2O_2 solution per mol of PbO_2 for 60 min at 20 °C, with 1/5 as the starting PbO_2 /water ratio, also resulted in the precipitation of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ compound at an acceptable recovery of 99%.

Experimental results for leaching–crystallization of $\text{Pb}(\text{C}_6\text{H}_6\text{O}_7)\cdot\text{H}_2\text{O}$ by reacting the PbO and PbO_2 (and PbSO_4 reported in Part 2 by Sonmez and Kumar, 2009) with $\text{C}_6\text{H}_8\text{O}_7\cdot\text{H}_2\text{O}$ have shown that lead can be recovered effectively as lead citrate crystals. The lead citrate precursor, can be readily converted to PbO (containing some Pb) for directly making lead lead-battery pastes with controllable degree of metallization by a combustion–calcination process (Kumar et al., 2006, 2007). Energy for such a process is derived from the organics embodied in the precursor material. By controlling the calcinations process, it is also possible to obtain variation in the microstructure from nano- to micro-scale, nano-powders are attractive for future development work in advanced lead lead-acid batteries. A full process using the principles outlined in this paper is currently being commercialised.

References

- Ahmed, F., 1996. The battery recycling loop: a European perspective. *J. Power Sources* 59, 107–111.
- Andrews, D., Raychaudhuri, A., Frias, C., 2000. Environmentally sound technologies for recycling secondary lead. *J. Power Sources* 88, 124–129.
- Bellamy, L.J., 1980. *Advances in Infra-red Group Frequencies, the Infra-red Spectra of Complex Molecules*, vol. 2. Chapman and Hall, London.
- Bettle, G., Mills, H., Richter, E.B., 1982. *Process for Making Peroxycarboxylic Acids*. US Patent, No: 4314949.
- Burford, N., Eelman, M.D., LeBlanc, W.G., Cameron, T.S., Robertson, K.N., 2004. Definitive identification of lead (II)-amino acid adducts and the solid state structure of a lead-valine complex. *Chem. Commun.* 332–333.
- Diaz, G., Andrews, D., 1996. Placid – a clean process for recycling lead from batteries. *JOM* 48, 29–31.
- Ferracin, L.C., Chácon-Sanhueza, E.C., Davoglio, R.A., Rocha, L.O., Caffeu, D.J., Fontanetti, A.R., Rocha-Filho, R.C., Biaggio, S.R., Bocchi, N., 2002. Lead recovery from a typical Brazilian sludge of exhausted lead-acid batteries using an electrohydrometallurgical process. *Hydrometallurgy* 65, 137–144.
- Forrest, H., Wilson, J.D., 1990. Lead recycling utilising short rotary furnaces. In: Mackey, T.S., Prengaman, R.D. (Eds.), *Lead-Zinc'90, Proceedings of a World Symposium on Metallurgy and Environmental Control*, sponsored by the TMS Lead, Zinc, and Tin Committee and Held During the 119th TMS Annual Meeting, February 18–21, Anaheim, California, pp. 971–978.
- Gong, Y., Dutrizac, J.E., Chen, T.T., 1992. The conversion of lead sulphate to lead carbonate in sodium carbonate media. *Hydrometallurgy* 28, 399–421.

- Habashi, F., 1997. Part three, primary metals: 9 Lead. Handbook of Extractive Metallurgy, Volume II: Primary Metals, Secondary Metals, Light Metals. Wiley-VCH, Weinheim, pp. 581–640.
- Harrison, R.M. (Ed.), 2000. Pollution, 3rd Edition. Royal Society of Chemistry, UK.
- Harrison, P.G., Steel, A.T., 1982. Lead (II) carboxylate structures. *J. Organomet. Chem.* 239, 105–113.
- Kourgiantakis, M., Matzapetakis, M., Raptopoulou, C.P., Terzis, A., Salifoglou, A., 2000. Lead-citrate chemistry synthesis, spectroscopic and structural studies of a novel lead(II)-citrate aqueous complex. *Inorg. Chim. Act.* 297, 134–138.
- Kumar, R.V., Sonmez, M.S., Kotzeva, V.P., 2006. Lead Recycling, UK Patent Application No: 0622249.1.
- Kumar, R.V., Sonmez, M.S., Kotzeva, V.P., 2007. Lead recycling, PCT Patent Application No: GB2007/004222, filed on 8 November, 2007.
- Lin-Vien, D., Colthup, N.B., Fateley, W.G., Graselli, J.G., 1991. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules. Academic Press, Inc., London.
- Olper, M., 1993. A Full Electrochemical Approach in Processing Junk Batteries, EDP Congress. Proceedings of TMS Annual Meeting, Denver, Colorado, USA, February 21st–25th, pp. 959–966.
- Prengaman, D.R., 1980. Reverberatory furnace-blast furnace smelting of battery scrap at RSR. In: Cigan, C.M., Mackey, T.S., O'Keefe, T.J. (Eds.), Lead-Zinc-Tin'80, Proceedings of a World Symposium on Metallurgy and Environmental Control, Sponsored by the TMS-AIME Lead, Zinc, and Tin Committee at the 109th AIME Annual Meeting, February 24–28, Eds., Las Vegas, Nevada, pp. 985–1002.
- Prengaman, R.D., 1995. Recovering lead from batteries. *JOM* 47, 31–33.
- Prengaman, R.D., 2000. Lead product development in the next millennium. In: Dutrizac, D.M., Gonzales, J.A., Henke, D.M., James, S.E., Siegmund, J.A. (Eds.), Lead-Zinc 2000, The Minerals, Metals & Materials Society (TMS), Pennsylvania, pp. 17–22.
- Prengaman, R.D., Raymond, S., 1980. Method of Recovering Lead Values from Battery Sludge. US Patent, No: 4229271.
- Prengaman, R.D., Morgan, C., Hine, E., Homer, P., Griffin, G.M., 2001. US Patent, No: 6177056.
- Ramus, K., Hawkins, P., 1993. Lead/acid battery recycling and the new Isasmelt process. *J. Power Sources* 42, 299–313.
- Reynolds, R.M., Hudson, P.E., Hudson, E.K., Olper, M., 1990. Advances in lead-acid battery recycling: Engitec's automated CX breaker system. In: Mackey, T.S., Prengaman, R.D. (Eds.), Lead-Zinc'90, Proceedings of a World Symposium on Metallurgy and Environmental Control, Sponsored by the TMS Lead, Zinc, and Tin Committee and Held During the 119th TMS Annual Meeting, February 18–21, Anaheim, California, pp. 1001–1022.
- Sonmez, S.M., Kumar, R.V., 2009. Leaching of waste battery paste components. Part 2: leaching and desulphation of PbSO₄ by citric acid and sodium citrate solution. *Hydrometallurgy* 95, 82–86. doi:10.1016/j.hydromet.2008.04.019.